

Organic thin film transistors

Challenging the portable sensor technology

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Résumé

Le pari des transistors organiques en couche mince : application à la technologie des capteurs portables

La technologie des capteurs portables pour la détection des gaz et vapeurs fait de plus en plus appel aux transistors organiques en couches minces. Ils présentent de nombreux avantages par rapport aux capteurs classiques fondés sur l'utilisation de couches d'oxydes métalliques, qui fonctionnent à température élevée, et pour lesquels la sélectivité reste médiocre. Après avoir décrit le fonctionnement d'un transistor organique en couche mince, et les mécanismes de conduction et de transport de charge dans la couche organique de type polycristallin, il est montré qu'une amélioration considérable de la sélectivité est observée lorsque l'on remplace la couche mince active de nature inorganique par une couche mince organique à base de polymère conducteur. En particulier, lorsque la chaîne carbonée du polymère conducteur a été substituée par des groupes alkoxy, de fortes interactions dipolaires se produisent avec des vapeurs d'alcool, conduisant à un signal relativement intense. Au contraire, si la même chaîne carbonée est modifiée par des groupes alkyles apolaires, l'interaction avec la vapeur d'alcool reste faible et le signal est de faible intensité. Il est d'une plus grande amplitude si l'analyte est lui-même de nature apolaire, ce qui illustre la bonne sélectivité de tels capteurs.

Mots-clés

Transistor organique en couche mince, détecteur de gaz, reconnaissance des odeurs, nez électronique, couches organiques actives, transduction sélective, polymères conducteurs.

Abstract

Organic thin film transistors are increasingly being used for the implementation of a miniaturized portable system for the detection of gases and vapors. They present numerous advantages compared to traditional transistors, whose technology is based on the use of layers of metallic oxides which function at a high temperature and whose selectivity remains mediocre. After describing the way in which an organic thin film transistor functions, with particular focus on the description of methods of conduction and transport of charge in an organic polycrystalline thin film, it is shown that a substantial improvement in selectivity is achieved when one replaces the inorganic thin film with an organic thin film made of conducting polymers (CPs). In particular, when the carbon chain of the conducting polymer has been substituted by alkoxy groups, strong dipolar interactions occur with alcohol vapors and result in a relatively intense reading. Conversely, if the same carbon chain is modified by non-polar alkyl groups, the interaction with the alcohol vapor remains weak and the signal is of low intensity. It achieves even greater amplitude if the analyte is itself non-polar, which clearly illustrates the good selectivity of such transistors.

Keywords

Organic thin film transistor, gas sensors, odor recognition, e-nose, active organic layers, selective transduction, conducting polymers.

The first demonstration of an OTFT chemical sensor dates back to the late 1980s [1-2], a few years after the first organic thin-film transistor (OTFT) was proposed. Very soon, OTFT sensors showed their great potential in overcoming the commonly used electrical gas sensors such as chemiresistors. In fact, the implementation of a miniaturized portable system for the detection of volatile analytes, performing in terms of sensitivity, selectivity, reliability and costs, is still an open challenge that commercially available sensors are not yet able to satisfy. Currently commercialized electrical gas sensors, such as metal-oxide based chemiresistors, offer great stability but rather poor selectivity. One of the main drawbacks is their high operating temperature that makes their implementation in battery operated portable systems difficult. Even though their selectivity can be greatly enhanced by switching to organic active layers, reliability of organic chemiresistors is still an issue. Aside from this, another need of the sensor industry is to develop portable devices for complex

odor recognition, such as cheeses, beers, olive oil and also explosives or pathogen bacteria. This task is currently addressed by sensor array systems that attempt to mimic the mammalian olfactory system, the so called "e-noses" (electronic noses) [3-4]. The potential of e-noses to fulfill the needs of food and beverage control as well as of medical diagnostic and public security is enormous. Several commercial applications of this new technology have already been achieved [5] but they do not yet perform at the level required by consumers, since miniaturization as well as cost effective production are still issues. Here we show that the implementation of OTFT sensors could be very beneficial in order to overcome chemical sensor limitations. Operated as multi-parameter sensors, OTFTs offer a viable alternative to currently commercially available sensors. They show very high repeatable as well as fast and reversible responses [6], can be operated at room temperature and demonstrate good selectivity towards a broad range of analytes [7].

What's new in OTFT

The novelty of OTFT sensors can be easily understood by comparing OTFT to common electrical gas sensors. Currently commercialized sensing instruments are, indeed, of two main types: metal-oxide resistive sensors and inorganic field-effect sensors. E-noses, on the other hand, are array-based systems that, to date, are manufactured by using conducting polymers (CP)-based sensors in sensing active matrix.

Metal-oxide based chemiresistors are schematically shown in *figure 1a*. There are two-terminal devices employing gas-sensitive metal-oxide active layers such as for example SnO₂ and ZnO [5, 8-10]. When the chemiresistor is in normal air, the oxygen present in the air oxidizes the active layer, removing electrons from the bulk of the metal-oxide semiconductor. The free carrier concentration is then reduced, with a consequent decrease in conductivity. When the metal-oxide film is exposed to a reducing analyte, it removes oxygen at the interface, injecting electrons into the semiconductor and resulting in a conductivity enhancement. The gas analyte is detected by means of a single parameter response, namely the change in the metal-oxide semiconductor active layer bulk resistivity. Chemiresistors present the great advantages of high response stability and good sensitivity, but they also present many drawbacks. Due to the redox nature of the interactions taking place between the analyte molecule and the metal-oxide active layer, such sensors are not very selective towards different odor molecules. At the same time, high operation temperatures are needed in order to release the gas molecules bonded to the metal oxide and restore the original sensor condition after the analyte is removed. Selectivity issues of chemiresistors can be solved by implementing organic active layers such as CPs, instead of metal-oxide films [5, 11]. CP chemiresistors can give sensitivities over a broad range of organic compounds. Moreover, CPs are cost effective and easily synthesized. They also offer fast responses to a large number of volatile analytes with low power consumption. Nevertheless, reliability in CP-based chemiresistors is still an issue, as well as sensitivity to humidity and long-term drift.

Inorganic field-effect gas sensors, also known as chemically sensitive field-effect transistors (CHEMFETs), are schematically shown in *figure 1b*. They are silicon-based MISFET (metal-insulator semiconductor field effect transistor) top gate transistors with their gate contact as sensing element [9, 12-17]. They have been successfully commercialized as highly sensitive hydrogen sensors for many years and are mainly used as leak detectors, showing very reliable responses. The FET (field-effect transistor) channel material is usually made of crystalline silicon underneath the gate contact and the gate dielectric layer; therefore, the charge transport in this region is not directly affected by the exposure

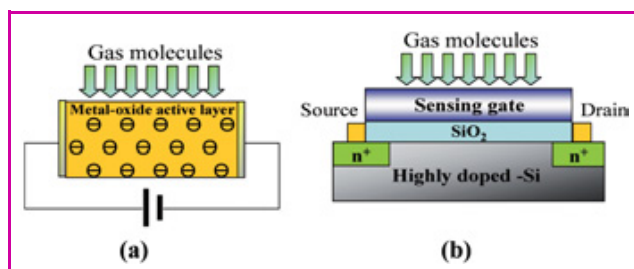


Figure 1 - (a) Schematic overview of a metal-oxide chemiresistor; (b) CHEMFET (chemically sensitive field-effect transistor) typical structure.

to the analyte. The transduction principle is based on the linear relationship existing between the transistor threshold voltage, V_t , and the difference between the gate material and the semiconductor work functions [16]. Upon gas exposure, a change of the work function, in each of these materials or in both, can take place and the response to the odor molecule is given by a single parameter signal, namely the variation of the CHEMFET V_t . Hydrogen detection down to the parts per billion range have been obtained with inorganic CHEMFET. Nevertheless, sensitivity and selectivity of such devices to different organic vapor are not very high and both depend on the gate materials and on the operating temperature (in the 50-200 °C range). As in the case of chemiresistors, the selectivity properties of CHEMFETs were broadened by using different conducting polymers as gate materials [14]. The main advantage of CP based CHEMFET is the ability to detect V_t changes by passing a very low current through the conducting polymer. This makes CHEMFETs more stable than chemiresistors. Detected concentrations are still in the high parts per million range and responses are fairly reversible.

A schematic representation of a sensing OTFT is given in *figure 2*. OTFT sensors are bottom gate field effect transistors employing polycrystalline organic active layer acting at the same time as the sensing membrane. They consist of a conductive silicon substrate covered by a thin dielectric film interfacing with the organic active layer. Source and drain contacts are defined by gold thermal evaporation through a shadow-mask over the organic active layer, while the gate contact is taken on the silicon substrate. As shown in *figure 2*, OTFTs are operated in the common source configuration, connecting the source contact to the ground and biasing the gate and the drain contacts against it. The gate bias, V_g , controls the current, I_d , flowing into the organic active layer between source and drain electrodes under an imposed bias, V_d .

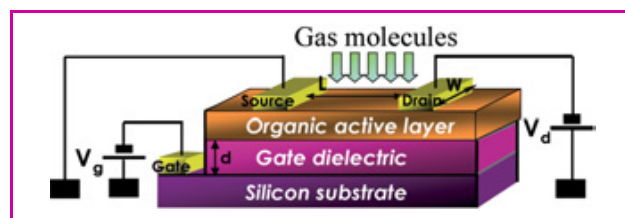


Figure 2 - Sensing OTFT (organic thin film transistor) structure.

When the OTFT is exposed to the analyte to be revealed, the odor molecules interact with the organic active layer, which thus behaves as sensing membrane as well. Such interaction can be revealed by monitoring the variation of current flowing in the OTFT organic channel. OTFT exposure to chemical analytes generally results in fast, room temperature and reversible responses to a wide range of organic molecules [7]. The three-terminal structure of OTFTs is particularly advantageous when they are employed as chemical sensors. As we will discuss, the OTFT structure enables one to operate in two distinct conduction modes depending on the V_d and V_g applied potentials. This makes it possible to operate OTFTs as multi-parameter sensors recording distinct responses in the two different operations modes. In addition, OTFTs have been proven to deliver gate dependent responses. Response enhancement of even two orders of magnitude can be obtained for different sensor/analyte systems at fixed concentrations by simply increasing the bias applied to the gate electrode. Another advantage of OTFT sensors is that they do not require high working temperatures since they can be reset by a proper biasing of the gate.

OTFT sensors are also highly reproducible, showing a recovery of the signal within 2% over several tens of repeat exposure cycles [7]. Finally, it has quite recently been demonstrated that it is possible to modulate selectivity of TFT (thin film transistor) sensors, by playing with the nature of the organic active layers and with the nature of their substituents [17].

OTFT sensors

Sensing and active layer materials

OTFT active layers are generally made of conducting polymers or oligomers, such as regioregular polythiophenes or pentacene molecules, deposited as films, several tens of nanometers thick. Different techniques are usually employed to deposit the film: solution casting, spin coating, Langmuir-Shäfer or Langmuir-Blodgett techniques for solution processed thin film and thermal evaporation for molecules with a low degree of solubility are the most common ones. *Figure 3* shows the chemical structure of some p and n-type organic semiconductors used as the active layer in OTFTs [18]. These organic active layers are generally polycrystalline in nature, exhibiting a granular morphology where each grain has linear dimensions of at most hundreds of nm and a crystalline-type degree of structural order.

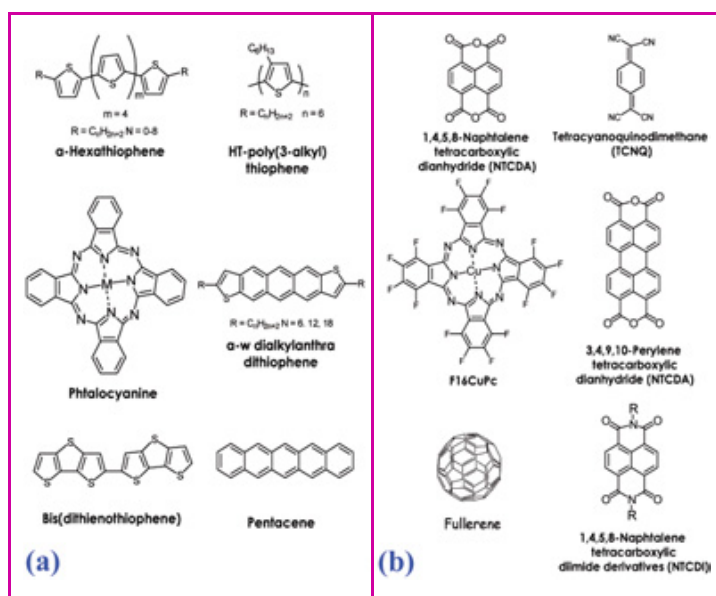


Figure 3 - Chemical structures of different (a) p type and (b) n type organic semiconductors employed as OTFT (organic thin film transistor) active layers [18].

OTFT operation

The electrical behavior OTFTs is characterized by current-voltage (*I-V*) curves such as those reported in *figure 4*. Each of these curves is measured at a fixed gate bias, V_g , swiping the difference of potential applied between source and drain, V_d . The range of voltages employed depends on the device geometry, namely on its channel length (L , distance between source and drain electrodes), its channel width (W , source and drain pad width) and the thickness of the gate dielectric, d (see *figure 2*). The curves of *figure 4*, like those recorded for inorganic TFT, show a linear region (I_d) at V_d bias much lower than $(V_g - V_t)$ and a saturation region ($I_{d,sat}$) at V_d bias much higher than $(V_g - V_t)$, where V_t is the transistor threshold voltage.

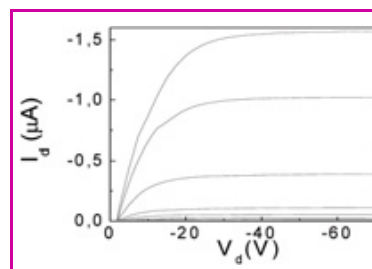


Figure 4 - Current-voltage (*I/V*) curves at different gate bias for a pentacene based OTFT (organic thin film transistor).

The analytical expression generally used to describe the OTFT *I-V* curves are the same derived for standard inorganic TFT [19-20]. These are given in the following:

$$I_d = \frac{W}{L} \mu C_i \left(V_g - V_t - \frac{V_d}{2} \right) V_d \quad V_d \ll (V_g - V_t) \quad (1)$$

$$I_{d,sat} = \frac{W}{2L} \mu C_i (V_g - V_t)^2 \quad V_d > (V_g - V_t) \quad (2)$$

$$V_t^{TFT} = \frac{qNd}{C_i} \quad (3)$$

where μ is the field effect mobility of the charge carriers and represents the charge drift velocity in the organic layer per field unit, and C_i is the dielectric capacitance for unit area.

The equations reported above are valid only when the charge carrier FET mobility is a constant, which is not the case for polycrystalline OTFTs where the mobility is gate field dependent. The inorganic TFT equations are then generally used only to give an estimate of important device parameters such as the field effect mobility and the threshold voltage.

Typical values of field effect mobility, μ , for organic materials are in the 10^{-2} - 10^{-1} cm^2/Vs range, but values as high as 1-10 cm^2/Vs can be measured with active materials such as pentacene [18]. These figures are comparable to those reached with inorganic TFT materials such as a-Si:H, characterized by mobilities of 0.1-1 cm^2/Vs . Another figure is the *on/off* ratio, defined as the ratio of the current in the "on" and "off" states. This is indicative of the switching performance of the device from the on to the off state. *On/off* ratios as high as 10^6 have been obtained for OTFT devices. Another important parameter is the threshold voltage, V_t , that is ideally seen as the gate voltage inducing an OTFT channel conductance (at low V_{ds} voltages) equal to that of the bulk organic semiconductor and in fact marks the passage from the "off" to the "on" conductivity regime. It is also related to the organic semiconductor trap density, as it corresponds to the voltage required to fill trap states in the organic material or at the interface with the gate dielectric [21, 22]

OTFT sensing mechanism

The sensing element of an OTFT sensor is its organic active layer. This is generally a polycrystalline film usually described as formed by contiguous grains having a crystalline core and amorphous grain boundaries. In *figure 5* one can see the AFM (atomic force microscope) micrograph of two contiguous grains of a pentacene active layer. The polycrystalline nature of the active layer strongly influences both the conduction and sensing mechanisms of these devices.

The charge transport in organic materials is modeled as the result of the contribution of two phenomena: an inter-grain charge transport and the conduction across grain boundaries both indicated in *figure 5*. In addition, a thermally activated transport mechanism such as the multiple trapping and

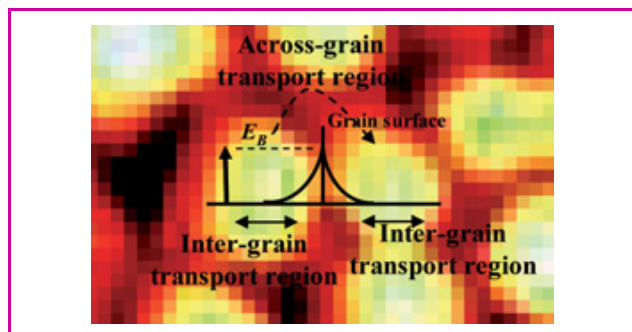


Figure 5 - Schematic diagram of the potential barriers at grain boundaries of the OTFT (organic thin film transistor) sensing layer.

thermal release (MTR) model, widely used to model transport in a-Si:H TFTs, is generally applied to describe polycrystalline OTFTs at room temperature [19]. MTR models the organic films as systems with a narrow delocalized conduction band and a high concentration of localized lower energy electronic states situated in the gap, which act as low mobility trap states. Such traps can be due to impurities as well as to structural defects located in the crystalline grain and at the grain boundaries [23-24]. During the inter-grain transport, while moving from source to drain through the delocalized levels, charges interact with the localized levels, getting trapped and eventually thermally released, due to an activation energy of several tens of milli-electron volts. The mobility generally increases with increasing gate bias, since at low gate bias the induced charges are mostly trapped in low mobility states. As the bias is increased, the Fermi level at the insulator/organic interface reaches the closest band edge. At this point, the lower energy trap states are all filled, and the induced charges are now freer to move. Moving from source to drain, charges are also transported from a grain to another grain through grain boundaries. This transport is limited by the strength of the potential barrier between contiguous grains, as sketched in figure 5. The mobility across two grains separated by a grain boundary has been described as [24]:

$$\frac{1}{\mu} = \frac{1}{\mu_C} + \frac{1}{\mu_{GB}} \quad \text{with} \quad \mu_{GB} \propto \exp\left(\frac{E_B}{kT}\right) \quad \text{and} \quad E_B = \frac{e^2 n_t^2}{8\epsilon_r \epsilon_0 \rho} \quad (4)$$

where μ_C is the single crystal mobility, μ_{GB} is the mobility across the grain boundary, E_B is the potential barrier between the grains, ϵ_r is the dielectric constant of the semiconductor, ϵ_0 is the permittivity of vacuum, n_t is the surface density of charged traps at the grain boundaries, ρ is the carried density, and k and T are the Boltzmann constant and temperature respectively [24].

The conduction mechanism plays a crucial role in determining the sensing mechanism of an OTFT sensor. OTFT V_t and μ depend on the volume density of trapped charges and on the potential barrier between contiguous grains, respectively [24]. When exposed to several reactive species charge trapping-detrapping processes occur at the organic active layer, enhancing or lowering barriers between grains. V_t and μ are influenced by the interaction of the transistor active layer with a chemical species, and this result in a change of the device on-current. Many active layers such as substituted thiophene-based polymers and oligomers, naphthalenes, copper phthalocyanines and pentacene have been investigated in OTFT sensors, and different analytes, such as alcohols, ketones, thiols, nitriles, esters and ring compounds have been sensed with these systems recording on and off responses

[25]. In all of the above situations, the active layer-analyte interaction has been modeled as the analyte molecules being adsorbed at the surface of the grains [26]. Analyte molecules can also reach the interface with the gate dielectric through the voids between grains [27]. This is interesting because the strength of the interaction with the analyte increases with increasing the grain boundaries exposed to the odor molecule, thus demonstrating the crucial role played by the grain boundaries in the OTFT sensing mechanism [28-29]. During this process, the analyte molecules being trapped at the grains boundaries cause a change of the barrier potential height, E_B , changing the film mobility accordingly to equation (4). Besides trapping, a minor doping effect has been observed in specifically designed OTFT sensor/odor systems [27, 29].

OTFT selectivity

The recognition of chemical analytes by OTFT sensors is obtained by exploiting the interactions taking place at the odor molecules/OTFT's active layer interface. CP-based active layers are, indeed, organic films with very weak selectivity toward organic molecules such as alcohols or alkenes. On the other hand it has been recently demonstrated that it is possible to modulate their specificity by substituting the CP backbones with properly chosen functional groups [11]. In presence of the odor molecules, this induces a partitioning of the analyte molecules in the film, comparable to what happens to a stationary phase in a chromatographic column [30]. In this case the OTFT sensing mechanism involves surface-mediated weak interactions between the functionalized polymers and the analyte. The adsorption of the odor molecule on the organic film grains appears to be modulated by the degree of chemical affinity between the odor molecule and the polymer functional groups. A proper chemical functionalization of the organic material forming the active layer can result in a film which, through the surface of its grains, is able to control the partition coefficient of analytes into the active layer, improving OTFT selectivity [26, 31-33].

The interesting approach of using side-chain functional groups to confer broad selectivity to a chemical sensor was proposed for the first time by Hierlemann *et al.* [30] and demonstrated on a set of polysiloxanes. Alkyl-substituted CPs have subsequently been employed in a chemiresistor-type configuration to promote the detection of non polar vapors [11, 34], since such conductive layers are generally much more sensitive to polar substances. Recently different linear chains have been used both as substituents of polythiophene based sensing layers and as analyte molecules to study their influence on the selectivity of CP based sensing devices [26]. Polythiophenes substituted by alkyl and alkoxy side groups have been used as sensing layers in OTFT and quartz crystal microbalance (QCM) devices to sense different organic vapors such as alcohols, alkanes and ketones. Alkyl and alkoxy side chains strongly influence the polar character of the polymers, modifying their associated dipole moments. This is thought to work as a driving force during the interaction with the analytes. This becomes very apparent when looking at the QCM and OTFT responses of some alkyl and alkoxy substituted polythiophenes to controlled concentrations of ethanol and 1-hexanol vapors [26]. Figure 6 reports OTFT responses to ethanol and 1-hexanol alcohol vapors of a poly-didodecyl-terthiophene and a poly-dipentoxo-terthiophene. Similar responses have been reported using QCM sensors with the same active layers [31]. Both QCM and OTFT responses, taken at room temperature, are reversible and very fast,

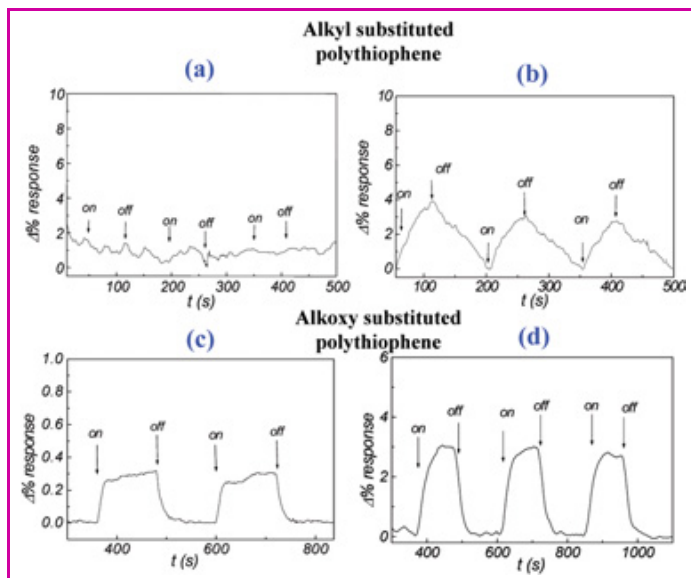


Figure 6 - OTFT (organic thin film transistor) responses to ethanol (a) and (c) and to 1-hexanol (b) and (d) for alkyl polythiophene and alkoxy polythiophene, respectively.

supporting the occurrence of a weak, surface mediated interaction. Exposure to a series of analytes always results in a mass up-take for QCM sensors and a current decrease for OTFT sensors [26]. This occurrence supports the hypothesis that the mass up-take, due to the physisorption of the analytes at the polymer grains, leads to an enhancement of the barriers between the grains, causing the current intensity to decrease. It is interesting, from the point of view of achieving selective behaviour, that no response can be detected with polythiophenes substituted with long alkyl chains exposed to ethanol for both QCM and OTFT sensors. This is probably due to the poor affinity between the strongly polar ethanol and the non polar alkyl chain attached to the polymer [26].

Responses of the same alkyl (non polar) and alkoxy (polar) polythiophenes QCM sensors to six different analytes (*n*-heptane, ethanol, 1-butanol, and 1-hexanol acetone and 2-propanol) have been recently reported versus the analyte dipole moment and the analyte molecular alkyl chain length [26]. The responses correlate linearly very well for the polar substrate. No clear trend is observed for the responses of the non-polar active layer, namely the alkyl polythiophene one, to the same analytes. On the contrary, good linear correlation can be observed between the responses of the alkyl chain-functionalized material and the length of the alkyl chain analytes. No correlation with the alkyl chain length can be seen for the polar active layer in this case. Polar-type interactions dominate in the case of the polar alkoxy polythiophene sensor, making this device more sensitive to such substances, whereas dispersion-type interactions can be better discriminated and recognized using alkyl polythiophene devices that are also more sensitive to long alkyl chain-bearing molecules than to shorter alkyl chain alcohols.

All this bears strong evidence as to the crucial role of functional side groups in driving the organic active layers recognition towards a series of different chemical analytes.

Conclusions

In the last few years, OTFT chemical sensors have been shown to be very promising portable sensors, overcoming the main drawbacks of traditional sensors. Their implementation

in array based sensing systems also seems to be an interesting potential application. OTFTs can indeed be operated as multi-parameter sensors with high reproducibility. At the same time, much evidence have been given as to how it is possible to modulate their specificity by properly choosing CP side groups. In this respect, many interesting recent advances have demonstrated OTFT bio-specificity. Experiments involving glucose and lactic acid detection by an α -6T TFT mediated by no specific receptors have been reported [31], as well as OTFT glucose sensors [33]. Poly(3,4-ethylene dioxythiophene)poly(styrene sulfonic acid) (PDOTPSS) thin-film transistors were also proposed for glucose sensing in a neutral pH buffer solution [32], while carbon nanotube nanoscale transistors have been proposed to detect protein binding via a biotin-streptavidin model system [35].

References

- [1] Laurs H., Heiland G., *Thin Solid Films*, **1987**, 149, p. 129.
- [2] Tsumura A., Koezuka H., Ando T., *Appl. Phys. Lett.*, **1986**, 49, p. 1210.
- [3] Persaud K.C., Dodd G.H., *Nature*, **1982**, 299, p. 352.
- [4] Gardner J.W., Bartlett P.N., *Electronic Noses: Principles and Applications*, Oxford Science Publ., **1999**.
- [5] Persaud K.C., *Materials Today*, April **2005**, 38.
- [6] Torsi L. et al., *Sens. Actuators B*, **2000**, 67, p. 312.
- [7] Torsi L., Dodabalapur A., *Anal. Chem.*, **2005**, 19, A, p. 77.
- [8] Wilson D.M. et al., *IEEE Sens. J.*, **2001**, 1, p. 256.
- [9] Janata J., Josowicz M., *Nat. Mater.*, **2003**, 2, p. 19.
- [10] Gardner J.W., Bartlett P.N., *Electronic noses: Principles and Application*, Oxford Science Publ., **1999**.
- [11] Bissell R.A. et al., *Phys. Chem. Chem. Phys.*, **2002**, 4, p. 3482.
- [12] Bergveld P., *IEEE Trans. Biomed. Eng.*, **1972**, BME-19, p. 342.
- [13] Lloyd Spetz A., Savage S., *Recent Major Advances in SIC*, W.J. Choyke, H. Matsunami, G. Pensl (eds), Springer, Berlin, **2003**, p. 879.
- [14] Janata J., Josowicz M., *Acc. Chem. Res.*, **1998**, 31, p. 241.
- [15] Bergveld P., Hendrikse J., Olthuis W., *Meas. Sci. Technol.*, **1998**, 9, p. 1801.
- [16] Bergveld P., *Sens. Actuators B*, **2003**, 88, p. 1.
- [17] Torsi L., Tanese M.C., Crone B., Wang L., Dodabalapur A., *Organic Transistor Chemical Sensors in Organic Field Effect Transistors*, Z. Bao & J. Locklin (Ed), CRC Press Taylor & Francis Group, **2007**, Ch. 6.2, p. 507.
- [18] Dimitrakopoulos C.D., Malenfant P.R.L., *Adv. Mater.*, **2002**, 14, p. 99.
- [19] Horowitz G., *Adv. Mater.*, **1998**, 10, p. 365.
- [20] Sze S.M., *Physics of Semiconductor Devices* (2nd ed), Wiley-Interscience, New York, **1981**.
- [21] Torsi L. et al., *J. Appl. Phys.*, **1995**, 78, p. 1088.
- [22] Horowitz G., Delannoy P., *J. Appl. Phys.*, **1991**, 70, p. 469.
- [23] Horowitz G., Hajlaoui M.E., *Synth. Met.*, **2001**, 122, p. 185.
- [24] Powell M.J., *Philos. Mag. A: Phys. Condens. Matter: Struct., Defects, Mech. Prop.*, **1981**, 43, p. 93.
- [25] Crone B. et al., *Appl. Phys. Lett.*, **2001**, 78, p. 2229.
- [26] Torsi L. et al., *J. Phys. Chem. B*, **2003**, 107, p. 7589.
- [27] Tanese M.C. et al., *Biosens. Bioelectron.*, **2005**, 21, p. 782.
- [28] Torsi L. et al., *J. Phys. Chem. B*, **2002**, 106, p. 12563.
- [29] Wang L., Fine D., Dodabalapur A., *Appl. Phys. Lett.*, **2004**, 85, p. 6386.
- [30] Hierlemann A. et al., *Anal. Chem.*, **2000**, 72, p. 3696.
- [31] Someya T. et al., *Langmuir*, **2002**, 18, p. 5299.
- [32] Zhu Z.-T. et al., *Chem. Commun.*, **2004**, 13, p. 1556.
- [33] Bartic C., Campitelli A., Borghs G., *Appl. Phys. Lett.*, **2003**, 82, p. 475.
- [34] Guernion N. et al., *Synth. Met.*, **2002**, 128, p. 139.
- [35] Star A. et al., *Nano Lett.*, **2003**, 3, p. 459.



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